

(12) UK Patent Application (19) GB (11) 2 271 087 (13) A

(43) Date of A Publication 06.04.1994

(21) Application No 9314993.8

(22) Date of Filing 20.07.1993

(30) Priority Data

(31) 922292
07970080

(32) 21.07.1992
02.11.1992

(33) CH
US

(71) Applicant(s)

Balzers Aktiengesellschaft

(Incorporated in Liechtenstein)

FL-9496 Balzers, Fürstentum, Liechtenstein

(72) Inventor(s)

Helmut Rudigier
Johannes Edlinger

(74) Agent and/or Address for Service

Saunders & Dolleymore
9 Rickmansworth Road, WATFORD, Herts, WD1 7HE,
United Kingdom

(51) INT CL⁵

G03F 1/08

(52) UK CL (Edition M)

B6J JMB1 JME JMH J501 J616 J70X J709
U1S S1918 S2061

(56) Documents Cited

None

(58) Field of Search

UK CL (Edition L) B6J
INT CL⁵ G03F
Online databases:WPI,CLAIMS

(54) Fabrication of a structural and optical element

(57) A structural optical element comprises a carrier substrate (1) as well as a layer system (3), with at least one dielectric layer (3H) stepped with respect to its thickness in at least one region opposite at least one second region. The dielectric layer is of the type MeO_x and is applied onto a base, where Me is a metal whose atomic mass is at least 44, and x is selected so that the coefficient of absorption of the layer material at light of wavelength $\lambda = 308 \text{ nm}$ is $k_{308} \leq 0.01$. The layer is built up through reactive etching by means of an activated gas for the step formation of the thickness. The etching can involve the sequential use of a gas not containing chlorine and a gas containing chlorine. The etching can be monitored by light reflection or by doping with alkali metal ions. Yttrium oxide can be used as an etch stop layer.

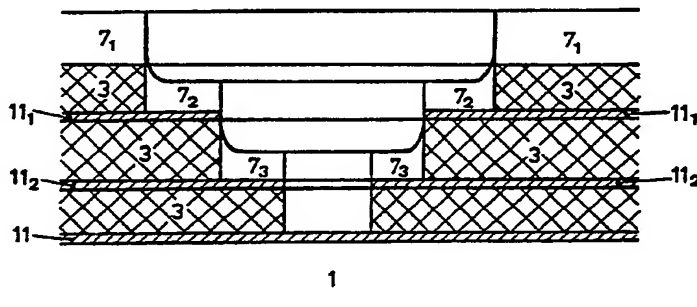
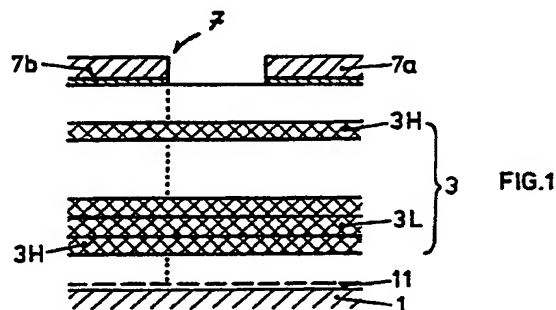
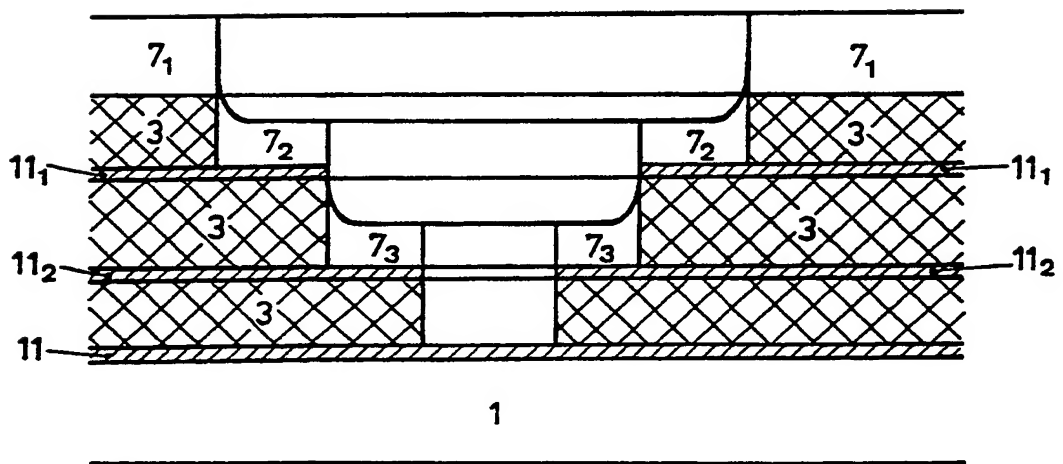
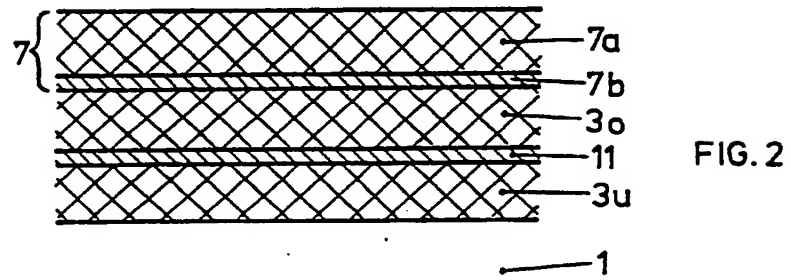
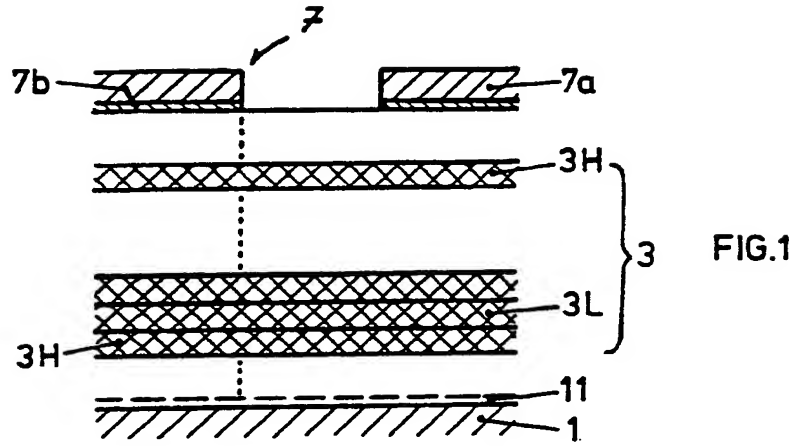


FIG.3

GB 2 271 087 A

1/4



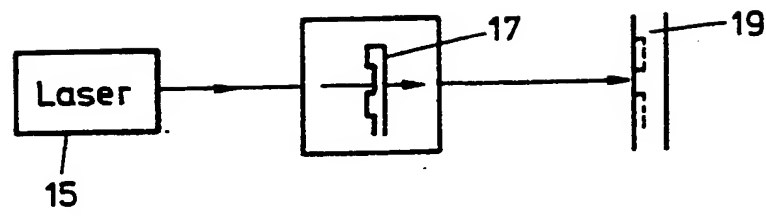


FIG. 4

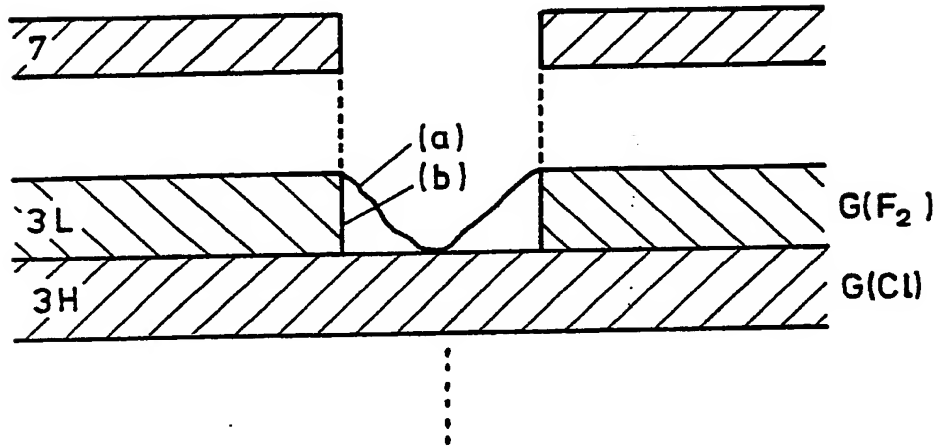


FIG. 5

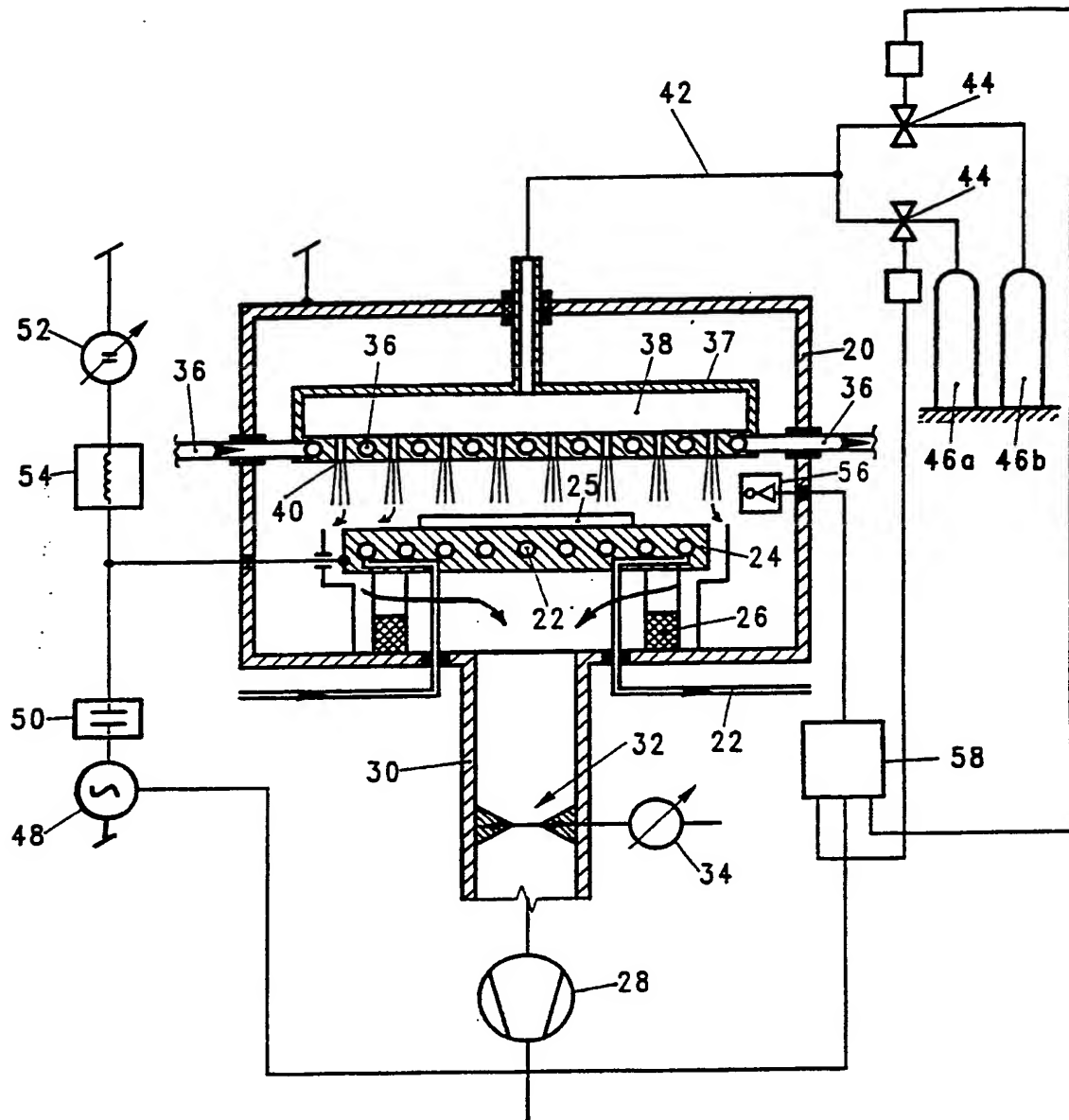


FIG.6

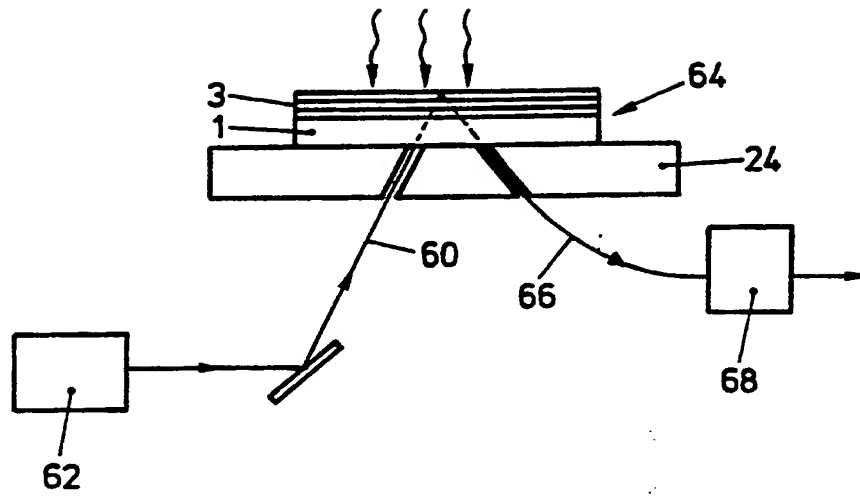


FIG. 7a

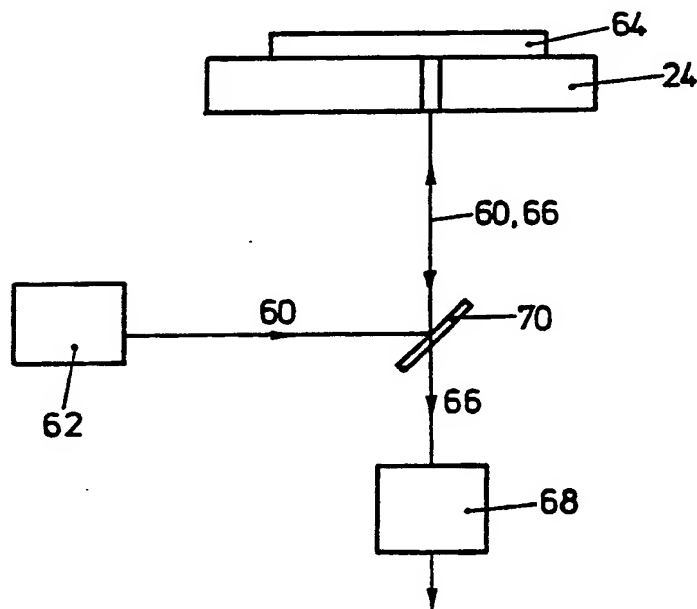


FIG. 7b

- 1 -

PROCESS FOR THE FABRICATION OF A STRUCTURAL
AND OPTICAL ELEMENT

FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to:

- a) a process for the fabrication of a structural element, in particular, an optical structural element;
- b) various types of optical elements;
- c) an optical imaging system;
- d) a vacuum treatment installation for the fabrication of an optical element;
- e) a process for tracking the erosion of material or the deposition of material;
- f) an installation for such tracking;
- g) a process for determining the point at which a surface has been reached during a reactive etching operation;
- h) an etching process control method; and
- i) a stop layer for an etching process.

Please refer to:

EP,A,0 463 319 (IBM)
EP,A,0 265 658 (IBM)
WO,A,9 101 514 (RAYCHEM)
EP,A,0 026 337 (IBM)
EP,A,0 049 799 (DAI NIPPON INSATSU)
THIN SOLID FILMS. Bd. 203, Nr. 2, 30. August 1991, Lausanne CH
Seiten 227 - 250
LEHAN ET AL 'Optical and microstructural properties of hafnium dioxide thin films', siehe Tabelle VI.

Although the process according to a), and, consequently, also the vacuum treatment installation according to d), are

suitable for the fabrication of a broad spectrum of structural elements each comprising a carrier substrate as well as at least one dielectric layer which, at at least one area, is to be eroded down to a given thickness, the gist or essence of the present invention is that it responds essentially to the requirements of semiconductor fabrication technology.

The structuring of dielectric layers, like structuring of metallic layers, is an essential process step in semiconductor technology. For the removal of dielectric layers of this type various methods have been used.

A first method, known as the lift-off technique, comprises the application of a photosensitive material, such as photoresist, to the substrate, exposing the material or resist to a desired pattern, developing the resist and then cleaning it. Depending on whether or not a positive or a negative resist has been used, the non-exposed or the exposed areas of the resist remain. A layer system is applied onto the substrate treated in this way, and subsequently the photosensitive resist disposed under the layers is dissolved by using an appropriate solvent. In this way, the layer system is removed in those regions of the substrate where the resist was remained. It is essential that the layer system does not impermeably close off the resist against the outside, especially at the edges of the region, in order not to preclude penetration by the solvent.

A second method comprises first applying the layer system onto the substrate. Subsequently the photosensitive resist is applied, exposed to the desired pattern, and developed. The layer system is thereby exposed at those sites or areas at which partial removal or removal down to the substrate is to take place. The latter takes place through bombardment by means of noble gas ions at typical energy values of 1000 eV and a typical ion current density of approximately 1 mA/cm². The layer material is thereby etched away as well as the

photosensitive resist. Since the etching rate of the resist is, in general, higher than that of the layer system, a thick resist has to be applied. This is done in order to prevent the resist from being etched away before the sites which are not covered by resist are removed down to the desired depth.

This process is also referred to as "ion milling" and is not selective in the sense that the etching rates for layer materials of the same type, such as for example of metal oxides, are not significantly different. An advantage of this ion milling method consequently resides in that it is not a process specific to the material to be etched.

A third method is reactive etching (RE). Departing from a layer system using a mask, for example made of a photosensitive resist as in ion milling, a gas is activated selectively, depending on the layer material to be removed, in the sense that reactive gas particles are generated which convert the layer material, which through the mask is exposed at particular sites, into volatile reaction products which are subsequently pumped off. In this way the layer system is removed or eroded. Through a suitable selection of the activated gas, called in the following a "reactive gas", it can be achieved that only a particular material is selectively and considerably etched whereby a high selectivity is achieved. By choosing a high selectivity with respect to the mask material, for example with respect to a photosensitive resist, only a thin layer of it need be applied. Also, the etching rates which can be achieved in reactive etching are by greater by decades than the rates achieved by ion milling. Consequently, this third method is in general economically more advantageous than is the ion milling process.

Activation of the reactive gas can take place in different ways, for example directly on the surface to be removed through laser beam bombardment or spatially distributed through laser

beam effect, microwave energy through ion or electron beams. Subsequently, the reactive gas activation can take place in a glow discharge whereby reactive species are formed.

While reactive etching through local laser effect can lead to high thermal loading of the layer system, those processes in which over the layer surface to be eroded an homogeneous density distribution of the reactive gas species is achieved, as is the case especially by means of a glow discharge, have the further essential advantage compared to the ion milling process that the edge profiles of the etched surface areas can be controlled better in the sense that practically ideal vertical steps can be achieved in the structure, if desired.

It is known from US Patent 4,684,436, to apply a pattern by means of a laser ablation process onto the surface of a work piece, there the intensity of a laser beam used during the process is modulated by means of a mask with a locally different layer system. The mask comprises a dielectric layer system on which, for achieving different energy transmission values through the above stated ion milling process, regions are etched to a greater or lesser depth or a number of the provided layers is selectively etched off. With respect to the layer stack structures of a mask of this type, which structures, as will become evident, can also be realized according to the present invention, US Patent 4,684,436 is incorporated here by reference.

It is further known from US Patent 4,923,772, to use excimer lasers for laser ablation processes, for example operating at a wavelength of 248 nm and wherein for the ablation process energy densities $> 100 \text{ mJ/cm}^2$ are required, and to use as a mask layer system with a highly reflecting dielectric layer stack which is stable with respect to high beam energy flows (laser damage threshold). The mask is made of a multi-layer stack, alternately with layers of high and low

refractive index materials. As the material with high refractive, hafnium oxide, scandium oxide, aluminum oxide or thallium fluoride is suggested. The surface removal on the mask layer stack is said to be realizable through an ion milling process or through glow discharge or through reactive ion etching, whereby, however, the glow discharge (plasma) or reactive ion etching is said to be slower and more difficult in the case of dielectric layers, due to the fact that the high-refraction material tends not to be reactive. Therefore, according to US Patent 4,923,772, the suggested layers of high refractive index material are structured by using ion milling or the lift-off technique.

SUMMARY OF THE INVENTION

It is the aim of the present invention to create a process of the initially stated type which is cost-effective in that a high etching rate and a high selectivity relative to the masking material, such as for example photosensitive resist and/or chromium, are achieved and thus thin resist layers, typically of 500 nm, can also be used for etching dielectric layers or layer stacks having great thicknesses. Further, the thermal load of the masking material, in particular of the photosensitive resist and/or chromium, remains low. Still further, improved control of the step profile is achieved in the sense that essentially vertical side walls are formed.

This is achieved when proceeding according to the method of the present invention.

In contrast to the explanation given in US Patent 4,923,772, it was found that the dielectric layers utilized according to the present invention are exceptionally suitable for reactive etching and are moreover materials which are highly refractive in the UV range. Because of the fact that

according to the present invention such dielectric layers can be etched reactively, a thickness patterning process with high selectivity and high etching rate for these materials becomes possible, including the above discussed advantages of reactive etching, and in particular for reactive ion etching, the high controllability of the slope of the side walls.

It is known from US Patent 4,440,841 to reactively etch TaO_x , i.e. $TaO_{1.5}$, wherein, however, in spite of the selection of tantalum as Me in the formula MeO_x , and $x=1.5$, the selection of x does not result in the low optical absorption of the material which is necessary for applications in the UV wavelength range $\lambda \leq 308$ nm, namely $k_{308} \leq 0.01$ or even correspondingly $k_{308} \leq 0.003$. For this notation, k refers to the extinction (absorption) coefficient. It should be emphasized here that although the MeO layers which are etched according to the present invention, are specified with their behavior in the UV range, this does not mean that they are only usable in the UV range. For example, due to their chemical resistance, the described and claimed layers or layer stacks are also to be used in other spectral ranges, in particular in the visible range.

In "Fabrication of mosaic color filters by dry-etching dielectric stacks", B. J. Curtis et al., JVac.Sci, Technol. A 4(1), (1986), p.70, a reactive etching process is described for SiO_2/TiO_2 dielectric layer systems. The mass of Ti is smaller than that of the metals among the dielectric materials according to the present invention, and, moreover, TiO_2 cannot be used for UV applications in the above stated spectral range or even for $\lambda \leq 350$ nm.

In a preferred embodiment of the process according to the present invention, the layer is created from Ta_2O_5 or from HfO_2 .

Furthermore, for many application purposes, such as for example for the fabrication of masks of the type represented in

US Patent 4,684,436, a layer system of the present invention is applied which comprises at least two of the dielectric layers of materials highly refractive in the UV range at wavelengths $\lambda \leq 351$ nm, in particular at wavelengths $\lambda \leq 308$ nm, together with layers of materials having low refractive index in this spectral range, such as for example SiO_2 layers.

Furthermore, according to the invention, a gas with a chlorine fraction is used as the gas to be activated, preferably at least comprising CHClF_2 , or in some cases He and/or CHF_3 and/or H_2 .

According to another embodiment of the invention, the high refractive index material can also be etched with a combination of the gases stated there.

If the at least one layer of high refractive index material, i.e. the MeO_x layer, before its removal is at least partially covered with a layer of low refractive index material, in particular SiO_2 , the extremely advantageous possibility is achieved that the stated high refractive index layer simultaneously acts as an etch stop layer in that the layer of low refractive index material is reactively etched with another gas, essentially without a chlorine fraction, so that the MeO_x layer is not etched at all or only to a negligible extent.

Although activation of the reactive gas according to the invention, can generally take place by means of charged particles, such as by means of electrons and/or ions, such as for example from a Kaufman source, and/or by photons or by laser enhanced means, activation of the gas is preferably carried out in a glow discharge in a vacuum chamber.

Moreover, the gas inlet is preferably cooled so that in addition to the cooling of the carrier surface for the fabricated structural element, a masking material, for example a resist, is not heated to an impermissible degree, which

subsequently makes possible a better detachment of the mask layer from the non-eroded surface regions of the dielectric layer.

5 In order to interrupt the etching process at the correct point in time, whether the layer system with the at least one dielectric layer has been eroded down to the substrate or if, in a multi-layer system the erosion has been carried out down to a given remaining layer system thickness, all known processes can be used, in particular one or several etch stop
0 layers can be incorporated directly on the substrate or between the layers of the multi-layer system, for example comprising Al_2O_3 . It has been found according to the invention, however, that an etch stop layer in particular of Y_2O_3 , is etched at a significantly lower rate than even an Al_2O_3 layer.

5 According to other features of the present invention, it has further been found that with the use of a surface of a material doped or provided with alkaline earth ions, a marked orange-colored glow is generated when the reactive ion etching by means of glow discharge reaches this surface. This effect
0 can be exploited very simply as a switch-off criterion for the etching process. A glass used in this way according to another feature of the invention has a markedly lower etching rate compared to the layer materials, and consequently acts automatically as the etch stop layer. In this way, an
3 impermissible deep etching into the glass substrate is prevented.

Furthermore, for monitoring the progress of the etching process the known reflection processes can also be used. Reference is made to the relevant explanations in US Patent
30 4,923,772, which in this respect, is incorporated by reference here.

According to another feature of the present invention, it is further suggested to direct at least one light beam from the

side of the structural element not exposed to the erosion through its substrate toward the layer and to draw conclusions about the remaining layer thickness from changes of the reflected beam. This has the essential advantage that the homogeneous introduction of a gas does not need to be impaired at the treatment side of the structural element for applying the beam of light and for retrieving the reflected beam. Furthermore, light applying and retrieving openings, potentially with light waveguides, are not exposed to the erosion process in that they are protected by the structural element itself.

An optical element according to another embodiment of the invention is formed as the structural element.

There is at least one layer on the structural element absorbs practically no light energy in the UV range with $\lambda \leq 308 \text{ nm}$, so that this structural element is highly suitable for use with UV lasers of high energy. Furthermore, the thickness layers ideally can be vertical to the particular layer surfaces which is realizable through the use of the reactive ion etching process.

An optical imaging system for achieving this forms another embodiment of the present invention.

According to a still further embodiment of the invention a laser source with a beam energy density of more than 100 mJ/cm^2 , preferably more than 200 mJ/cm^2 , and even more preferably more than 300 mJ/cm^2 , is used. This becomes possible due to the layer material MeO_x , whereby, due to the precise thickness stepping achieved by the reactive ion etching used according to the invention, the optical imaging system locally modulates the energy of the laser beam very accurately.

A vacuum treatment installation for the fabrication of the above stated structural or optical element, or for carrying out at least the etching step of the above stated fabrication

process, forms another embodiment of the invention.

A process for tracking the layer erosion and deposition from or on a structural element for transmitting light in at least one given spectral range is provided according to other features of the invention. A corresponding installation of the invention is also disclosed, according to which the stated tracking takes place through a reflection measurement which is carried out on the side of the structural element facing away from the deposition or erosion process.

The invention also includes a process for determining the point or instant at which the substrate has been reached by reactive ion etching, in which changes in the glow discharge light emission during etching of a surface doped with alkaline earth ions are exploited.

In particular it is therein utilized according to the invention, that a substrate of a glass with alkaline earth ions forms a surface of this type and consequently through the stated light emission detection it is possible to determine rapidly the point in time at which the etching process has locally reached the substrate.

According to other features of the invention, layers with high refractive index such as, in particular, the stated MeO_x layers are etched reactively by means of the one gas, in particular comprising the chlorine fraction. Layers of low refractive index, in contrast, are etched with other gases, such as gases comprising fluorine, in which the high refractive index materials are etched only to a strongly decreased degree. Thus it becomes possible, according to the invention, to etch a low refractive index layer with the stated other gas and to do this until the high refractive index layer has been reached, and still further until a complete homogeneous erosion of the low refractive index layer is reached in the desired area, because the high refractive index layer acts for the other gas

used, preferably essentially without chlorine fraction, as an etch stop layer. It is surprising that the high refractive index layers too, and this should be emphasized, are etchable with quite reasonable etching rates, also with fluorine-containing gases, in particular CHF_3 . Subsequently it is possible, with the introduction of the one gas, i.e. preferably with chlorine fraction, to continue etching of the high refractive index layer. By taking advantage of the stated selectivity, a complete large-area erosion of the low refractive index layer superjacent to the high refractive layer, is achieved.

According to a further embodiment of the invention, an optical element comprises a surface doped with alkaline earth ions, e.g. sodium, with which it becomes possible to detect the point at which the stated layer has been reached by the etching process during its fabrication on the basis of the glow discharge stimulated light emission.

According to a still further feature or embodiment of the invention, the stated surface is formed by a substrate glass comprising alkaline earth ions.

The various features of novelty which characterize the invention are pointed out with particularity in the claims annexed to and forming a part of this disclosure. For a better understanding of the invention, its operating advantages and specific objects attained by its uses, reference is made to the accompanying drawings and descriptive matter in which preferred embodiments of the invention are illustrated.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following the invention will be explained in conjunction with drawings wherein:

Fig. 1 is a partial sectional schematic view of a layer

system to b worked according to the invention with etching mask and etch stop layer on the substrate;

Fig. 2 is a view similar to Fig. 1 of an analogous layer system with embedded etch stop layer, for example in order to etch the layer system so that it is staggered at different depths;

Fig. 3 is a schematic sectional view of an optical element according to the invention, etched to staggered depths, with remaining etching mask parts still to be removed;

Fig. 4 is a schematic diagram of an optical imaging system according to the invention;

Fig. 5 is a schematic sectional view of a layer system fabricated according to the invention in which one of the MeO_x layers itself is used as an etch stop layer;

Fig. 6 is a schematic sectional view of a vacuum treatment installation according to the invention;

Fig. 7a is a schematic view of an etching depth or layer thickness detection system according to the invention per se, and used preferably in the installation according to Fig. 6; and

Fig. 7b is a schematic view of the system according to Fig. 7a, in which sent and reflected light beams are guided in a work piece carrier electrode through the same light waveguide channel.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Fig. 1 depicts a layer system 3 on a substrate 1. The layer system 3 comprises at least one high refractive index dielectric layer 3H, but is structured as a layer stack for most applications, with at least one low refractive index layer 3L also. The minimum configuration comprises substrate 1 and high refractive index layer 3H.

According to the invention, the high refractive index layer 3H comprises a dielectric compound MeO_x , where in:

Me is a metal of at least mass 44; and

x is selected so that the coefficient of absorption k, i.e. the extinction coefficient, of the layer material for light of $\lambda = 308 \text{ nm}$ becomes

$$k_{308} \leq 0.01,$$

preferably even

$$k_{308} \leq 0.003.$$

The layer 3H is thus also applicable for UV light wherein the low coefficient of absorption ensures that even at UV wavelengths $\leq 308 \text{ nm}$, high energies can be transmitted without the damage threshold of the dielectric material being reached.

As the low refractive index layer 3L preferably an SiO_2 layer is used or alternatively Al_2O_3 .

An etching mask 7, formed in known manner is superjacent to the uppermost layer 3H, which can comprise, for example, a photosensitive resist layer 7a and/or a metal layer 7b comprising Cr, Al or also Fe_2O_3 . The mask 7 is formed in known manner, i.e. developing of the photosensitive resist, etching of the metal layer or the like.

An etch stop layer 11, shown in dashed lines, in particular comprising Y_2O_3 , is intended to prevent etching of the substrate 1 during etching of exposed regions 3a which are yet. This is due to the selective effect of the reactive etching, according to which only the layer materials forming the layer system 3 are etched. An etch stop layer analogous to layer 11 can be incorporated into the layer system wherever the etching process is to be stopped or interrupted.

As a high refractive index material of layers 3H, Ta_2O_5 or HfO_2 are preferred according to the invention. These layer materials are exceptionally suitable for the stated application in the UV light range, but it is understood that they can also

b used with light of longer wavelengths. If the dielectric layer stack 3 is not to be eroded down to the substrate 1 through the reactive etching process, between an upper part of the layer system 3a and a lower part 3u, as depicted in Fig. 2, an etch stop layer 11 is inserted, comprising in particular Y_2O_3 . Y_2O_3 is particularly suitable for UV light at high power density, but also for applications in the visible light range. In the case where the dielectric layer stack is to be eroded to different levels, several etch stop layers 11 are used and, as is known, after reaching the first etch stop layer, by reapplying an etching mask, comprising for example a photosensitive resist and its development, regions are formed at the etch stop layer which are free of the reapplied mask layer, for example through corresponding etching or by means of a wet technique whereupon the subjacent dielectric layer stack 3 is continued to be etched until potentially a further etch stop layer has been reached, etc.

Metal layer 7b in Figs. 1 or 2 can potentially be omitted and the masking can be carried out by means of the photosensitive resist 7a only. Furthermore, after developing the resist layer 7a and etching away of the metal layer 7b, for example comprising chromium, the remaining resist layer can be removed and the remaining metal layer only can be used as the etching mask.

Fig. 3 depicts, by example, an optical element according to the invention, on which the dielectric layer system 3 has been eroded locally to two levels. The photosensitive resist 7, to 7, as well as the etch stop layers 11, and 11, are the last layers yet to be removed. An optical element according to the invention comprises as its minimum structure a substrate or carrier 1 as well as a layer 3H according to Fig. 1 and can be built up further with additional layers in known manner.

Due to the low absorption of the high refractive index

material used according to the invention, in particular Ta_2O_5 , or HfO_2 , optical elements of the invention are realizable with highly precise structuring edges which are highly suitable to be used together with UV lasers, excimer lasers of high energy, such as for example for the laser ablation technique in material working, in particular in semiconductor production. In that field energy densities of more than 100 mJ/cm^2 , preferably more than 200 mJ/cm^2 or even more than 300 mJ/cm^2 , are applied.

An optical imaging system according to the invention is depicted schematically in Fig. 4 and comprises an excimer laser light source 15, and an optical element 17 according to the invention, used as a mask in such a way that the pattern of the mask is transferred to a work piece 19 to be structured through laser ablation due to the mask-dependent locally varying laser energy transmission.

Fig. 5 illustrates a layer system with an etching mask 7, below which is a layer 3L of low refractive index material and a further layer 3H of high refractive index material. The layer 3H comprises the specific material MeO_x . The layer of low refractive index material, in turn, preferably comprises SiO_2 or alternatively, Al_2O_3 . The schematically depicted etching profile (a) represents the etching of layer 3L according to mask 7. This reactive etching takes place with a reactive gas G which preferably at least essentially does not comprise chlorine but rather fluorine. By means of the one reactive gas the layer 3H cannot be etched at all or only insignificantly. Consequently, this layer acts as the etch stop layer for the etching process of layer 3L.

In the case of a reactive etching process etching continues in spite of the fact that the surface of layer 3H with the preferably fluorine-containing reactive gas has been reached, until the layer 3L corresponding to mask 7 has been completely etched away from the surface of layer 3H. The

w rking process can now b compl ted if th re is n int ntion
 f etching th layer 3H also or the reactive gas is being
 changed in that now a different, preferably chlorine-containing
 gas is used, as is schematically indicated by G(Cl). The other
 process parameters can potentially also be changed.

Fig. 6 schematically illustrates a vacuum treatment
 installation according to the invention, laid out for
 performing the etching process to be completed within the scope
 of the process according to the invention. As has been stated,
 the structuring can in principle be carried out with different
 reactive etching processes within the scope of the invention.
 Preferably, however, reactive ion etching with the aid of a
 glow discharge is used. For this purpose the installation
 according to Fig. 6 comprises in a vacuum recipient 20 a work
 piece carrier electrode 24, which is water-cooled via a line
 system 22. The work piece carrier electrode 24 for a work piece
 25 is mounted so as to be electrically insulated with respect
 to the walls of the recipient 20, as is depicted schematically
 by insulation 26. Centrally under the work piece carrier
 electrode 24 is disposed a suction port 30 connected to a
 turbomolecular pump 28, whose pump cross section can be
 adjusted by means of an iris diaphragm 32 and via an adjustment
 unit 34 for the iris.

Opposing the work piece carrier electrode 24 is a counter-
 electrode 37 which is preferably water-cooled via a line system
 36. On its face opposing the work piece 25 are provided
 regularly distributed gas outlet openings 40 which communicate
 with a gas distribution system 38 and a gas feed line 42. The
 latter is connected via throughflow regulation valves 44 with
 one or several gas tanks 46a and/or 46b. With the setting
 valves 44 the particular throughflow quantity or the reactive
 gas composition is set or regulated. For reasons of
 cleanliness it is quite possible to implement the installation

vertically or with the work piece carrier electrode above.

As has been stated, the layers of high refractive index in the layer stack according to Figs. 1 to 3 are preferably etched with a chlorine-containing gas as the reactive gas. Consequently, the tank 46a, contain a chlorine-containing gas, preferably CHClF_2 , possibly additionally He or CHF_3 or H_2 . This tank 46a can, moreover, contain a combination comprising the gases Cl_2 , H_2 , F_2 or CF_4 , which gas mixture can also be supplied to the treatment chamber after being mixed from several gas tanks. The low refractive index layers, in particular of SiO_2 , on the layer stack according to Figs. 1 to 3 are also etchable by means of a reactive gas which essentially does not comprise any chlorine but rather, for example and preferably comprises fluorine, preferably fluorine gas.

Consequently, the second gas tank 46b according to Fig. 6 preferably contains the other gas which is not chlorine-containing but rather is a fluorine-containing gas. As will be explained in connection with Fig. 5, a layer of low refractive index material can be etched with the fluorine-containing gas from tank 46b, and after its etching-off down to the next lower high refractive index layer, the latter can subsequently be etched by supplying another, preferably chlorine-containing gas into a process volume P in the vacuum chamber 20.

In the case of the depicted example the work piece carrier electrode 24 is fed by means of an RF generator 48 via a matching network 50, relative to ground, to which is also connected, for example the chamber wall 20. In order to bias the work piece carrier electrode via a decoupling network 54, a settable DC value from a DC voltage source 52 can be added to the RF signal.

The electrical connection can, of course, also be carried out differently in known manner in that the AC signal is applied between work piece carrier electrode 24 and electrode

37 and the chamber wall 20 is placed independently of the electrode potentials, at a floating potential or at a reference potential. Independently of this, the work piece carrier electrode can still be connected to a DC bias voltage.

5 As has been explained, in the reactive etching process used according to the invention, it is an essential purpose is to detect at what moment the erosion of the layer stack on the substrate 1 according to Figs. 1 to 3, reaches a given degree. To this end, as schematically depicted in Fig. 6, a detector
10 unit 56 is provided which detects, in a manner to be described, when a given erosion depth has been reached and intervenes via an evaluation unit 58 in a controlling manner in the etching process. This intervention may occur, as depicted, in the RF generator 48 and/or the throughflow setting valves or elements
15 44 for the reactive gas or the reactive gases.

In particular it is therewith possible after etching of the low refractive index layers with the one gas, preferably with the gas not containing chlorine but rather preferably the
20 fluorine-containing gas from the tank 46b, to change the reactive gas, preferably by introducing at least a chlorine fraction or the stated chlorine-containing gas and, as was explained with Fig. 5, to etch the high refractive index layer of MeO_x . In general, the results of the present invention give so that with good probability of success, the stated
25 selectivity is achieved through the suitable selection of the Cl_2 or F content as well as possible additional gas fractions.

If, as has been described in conjunction with Fig. 1 to 3, etch stop layers 11 are provided in the reactive ion-etched layer stack according to the invention, the detector unit 56
30 detects for example changes in process radiation. In this connection it was found that if a glass with alkaline earth ions is used as the substrate material, when the etching process has reached the substrate, light is generated with a

significant spectral component, namely orange light, so that when using a substrate of this type the substrate can be used simultaneously as an etch stop layer, the point when the substrate is reached being readily detected.

5 Generally and furthermore, surfaces can be provided on the layer system which are doped with alkaline earth ions in order to detect in the stated manner, in conjunction with the glow discharge light spectrum which changes significantly, the moment when this surface is reached by the etching process. It is understood that the doping of the stated surface with alkaline earth ions takes place as a function of whether or not such a doping can be tolerated for the later application of the structural element which is fabricated according to the invention. For example, an alkaline earth ion doping, whether of the substrate, such as the substrate glass, or of a stack layer, in particular of a low refractive index layer, such as an SiO_2 layer, can lead to the result that the finished optical element is no longer optimally suitable for UV. But since, as has been stated already, the optical elements with the MeO_x layer worked according to the invention are not only suitable for UV use only but rather can also be quite advantageously used in the visible light range also, the stated doping in many cases will not degrade the required optical characteristics.

It is noted that the stated MeO_x materials, in particular HfO_2 , are chemically extraordinarily stable and, produced for example through ion plating, have an extremely low scattered-light component so that the use of these layers is often highly advantageous even with these optical elements being used in the visible light range.

When using a substrate material comprising glass with alkaline earth ions, for example sodium ions, it was further found that the etching rate of this substrate is significantly lower than that of the dielectric layers MeO_x used according to

th invention or the preferably used low refractive index layers, such as for example of SiO_2 or possible Al_2O_3 , so that additionally, when applying a substrate material of this type, it is ensured, that the substrate surface before interruption of the etching process when detecting the characterizing glow discharge light spectral component, is etched only to a small degree.

For monitoring the etching process with respect to the remaining layer or layer stack thickness, other known processes can also be used such as for example known reflection measurement of a laser beam which is guided, for example, through the electrode 37 onto the etched structural element and whose reflection is evaluated.

Moreover, methods such as plasma emission spectroscopy or mass spectroscopy of the pumped-off gases can be used for process control.

A preferred procedure for process guidance is depicted schematically in Figs. 7a and 7b, based on the representation of Fig. 6. This procedure or a correspondingly designed vacuum treatment installation are viewed as being inventive by themselves and also isolated from the complex for etching dielectric layers. With respect to Fig. 6, the beam 60 of a light source shown in Fig. 7a, preferably a laser light source 62, is transmitted through the work piece carrier electrode 24 and directed onto the structural element 64 which itself is transmitting in the spectral range of the light beam 60. The surface of the structural element is subjected to the erosion process or is more generally being worked, e.g. is being coated. The beam 66 reflected by the structural element 64 or the beams 66 reflected by the several layers are supplied for example via light waveguides to an evaluation unit 68. Changes of the beam reflection on the structural element 64 are evaluated as a measure of which of the layers have been eroded

up to that moment through the etching process, or which layer thickness has been deposited up to then, for example by means of a plasma-enhanced CVD process.

As depicted in Fig. 7b, this technique can also be implemented so that by means of a semipermeable mirror element 70 the reflected beam 66 is supplied to the evaluation unit 68 which acts upon the reactive gas setting elements and/or the RF generator (e.g. 13.56 MHz) 48 according to Fig. 6, within the scope of the etching process according to the invention. It must be emphasized that, depending on the etching process performed, upon reaching a given etching depth at which a changed layer material is encountered, this, after detection at the unit 68, may also be used for changing the reactive gas mixture, as has been stated, and that by this invention it appears probable, for a change from the chlorine-containing to the fluorine-containing gas and conversely, or for a change between other gases.

In the following examples of the process according to the invention will be represented as well as structural elements according to the invention.

In the examples the following notation is used:

L: layer of low refractive index material,

H: layer of high refractive index material,

optical thickness = (index of refraction) * (physical thickness x), and

x: physical thickness.

The diameter of the work piece carrier electrode 24 according to Fig. 5 is 25 cm, the distance d between work piece carrier electrode and counter electrode 37 is specified in each instance under the etching parameters.

Example 1

Ta₂O₅/SiO₂ Stack mirror, centered for 308 nm:

<u>Sequence</u>	<u>Material</u>	<u>Physical thickness x</u>
-----------------	-----------------	-----------------------------

5 Substrate

L ₁	SiO ₂	106 nm
H ₁	Ta ₂ O ₅	30 nm
L ₂	SiO ₂	91 nm
H ₂	Ta ₂ O ₅	30 nm

.0 -----
L SiO₂ 53 nm

} 4 x

H Ta₂O₅ 33 nm

.5 L₃ SiO₂ 106 nm

Structure: L₁H₁L₂H₂(LH)⁴L₃

Total thickness, physical: 707 nm

Etching parameters:

Reactive gas:

CHClF₂, He

Gas flow:

CHClF₂ : 50 sccm

He : 50 sccm

Gas pressure:

p = 1.8 x 10⁻³ mbars

RF power:

300 W

Frequency:

13.56 MHz

Electrode distance:

d = 5 cm

Etching time to substrate:

τ = 657 seconds

Average etching rate:

1.08 nm/sec

Externally applied

DC bias:

0 V

Note:

Including etching of Cr mask

Example 2

Stack mirror centered for 248 nm:		
<u>HfO₂/SiO₂</u>	<u>Material</u>	<u>Physical thickness x</u>
<u>Sequence</u>		
Substrate		
5 L ₁	SiO ₂	83 nm
H ₁	HfO ₂	29 nm

L	SiO ₂	42 nm
		} 7 x
10 H	HfO ₂	
		29 nm

Air

Structure: L₁H₁(LH),

Total thickness, physical: 609 nm

Etching parameters:

Reactive gas: CHClF₂
 Gas flow: 50 sccm
 Gas pressure: $p = 7 \times 10^{-3}$ mbars
 RF power: 300 W (13.56 MHz)
 Electrode distance: $d = 5$ cm
 Etching time: $\tau = 1098$ seconds
 Etching rate: 0.555 nm/seconds
 Externally applied
 DC bias: 0 V
 with 1 μ m AZ 1350 photosensitive resist mask

Example 3Single layer Ta_2O_5 Etching parameters:

	Reactive gas:	CHClF_2
5	Gas flow:	50 sccm
	Gas pressure:	$p = 1.2 \times 10^{-2}$ mbars
	RF power:	500 W (13.56 MHz)
	Externally applied	
	DC bias:	0 V
10	Electrode distance:	$d = 5$ cm
	Etching rate:	0.95 nm/seconds

Example 4Single layer HfO_2 Etching parameters:

	Reactive gas:	CHClF_2
15	Gas flow:	50 sccm
	Gas pressure:	1.1×10^{-2} mbars
	RF power:	300 W (13.56 MHz)
	Externally applied	
20	DC bias:	0 V
	Electrode distance:	$d = 5$ cm
	Etching rate:	0.39 nm/seconds

Example 5

Single layer Y_2O_3 (as etch stop layer!)

Etching parameters:

Reactive gas: $CHClF_2$, He
 Gas flows: $CHClF_2$: 50 sccm
 He : 69 sccm
 Pressure: 1.2×10^{-2} mbars
 RF power: 300 W (13.56 MHz)
 Externally applied
 DC bias: -80 V
 Electrode distance: $d = 5$ cm
 Etching rate: 0.06 nm/seconds

Example 6

Single layer, as low-refraction layer in stack: Al_2O_3

Etching parameters:

Reactive gas: $CHClF_2$, He
 Gas flows: $CHClF_2$: 50 sccm
 He : 69 sccm
 Pressure: 1.2×10^{-2} mbars
 RF power: 500 W (13.56 MHz)
 Externally applied
 DC bias: -97 V
 Electrode distance: $d = 5$ cm
 Etching rate: 0.41 nm/seconds

It must be emphasized that instead of the preferred reactive ion etching by means of glow discharge, in principle other reactive etching processes, such as for example "chemically assisted ion beam etching" are also suitable. Therein argon ions from a Kaufman ion source bombard the structural element to be fabricated thereby spraying a reactive gas, preferably $CHClF_2$, onto the surface of the element.

Furthermor , with the same arrangement according t Fig. 6, as has already been stated, th L layers, in particular comprising SiO_2 , can be etched with a different gas, for example with SF_6 , i.e. with a gas without chlorine fraction, wherein subsequently the H layers act as etch stop layers.

While specific embodiments of the invention have been shown and described in detail to illustrate the application of the principles of the invention, it will be understood that the invention may be embodied otherwise without departing from such principles.

CLAIMS

1. Process for the fabrication of a structural element, having a carrier substrate and a layer system on the substrate, the layer system including at least one dielectric layer which is stepped with respect to its thickness in at least one region as compared to a thickness of at least one second region of the dielectric layer to form at least one step in thickness, the process comprising:

applying a dielectric layer of MeO_x onto a base of the substrate, Me being a metal whose atomic mass is at least 44, x being selected so that the coefficient of absorption k of the layer material at light of wavelength $\lambda = 308 \text{ nm}$ is

$$k_{308} \leq 0.01; \text{ and}$$

building up the layer system using reactive etching by means of an activated gas to form the step in thickness in the dielectric layer.

2. Process according to Claim 1, wherein x is selected so that $k_{308} \leq 0.003$.
3. Process according to Claim 1, wherein Me is Ta and x is 2.5, the dielectric layer being applied being Ta_2O_5 .
4. Process according Claim 1, wherein Me is Hf and x is 2, the dielectric layer being applied being HfO_2 .
5. Process according to Claim 1, wherein the layer system comprises a layer stack on the substrate, the stack being

eroded in a stepped manner for the formation of the at least one step in thickness.

6. Process according to Claim 1, wherein the gas which is activated for the etching is CHClF_2 .

5 7. Process according to Claim 6, wherein the gas to be activated further includes at least one of He , CHF_3 , and H_2 .

8. Process according to Claim 1, wherein the gas to be activated for the etching comprises a combination of Cl_2 , with at least one of the further gases H_2 , F_2 , CF_4 , and SF_6 .

9. Process according to Claim 1, including, before the etching step, covering the dielectric layer at least partially with a further layer of low refractive index material as compared to the dielectric layer, and reactively etching the further layer with an activated further gas which is essentially without a chlorine fraction and which has a fluorine fraction which etches the MeO_x layer at a substantially reduced rate compared to an etching rate of the further gas on the further layer.

10. Process according to Claim 1, wherein further layers are provided in the layer system and including further etching the further layers with a gas which is essentially free of a Cl_2 fraction in such a way that the at least one MeO_x layer in the layer system acts for the further etching process as an etch stop layer.

11. Process according to Claim 1, including homogeneously

distributing the activated gas using a nozzle over a surface region to be etched, the gas being distributed substantially vertically onto the surface region, a density of reactive gas species in the activated gas being selected to be substantially homogeneous near the surface region.

12. Process according to Claim 1, including activating the activated gas using at least one of the charged particles selected from the group consisting of electrons and ions.
13. Process according to Claim 1, including enhancing the etching step using ultraviolet photons.
14. Process according to Claim 1, including providing a carrier electrode for the structural element and a counter-electrode spaced from the carrier electrode, maintaining a glow discharge between the carrier electrode and the counter-electrode for activating the gas, and supply the gas to the structural element using a nozzle for directing the gas substantially in the direction of the discharge.
15. Process according to Claim 1, including supplying the gas through a gas inlet and cooling the gas inlet.
16. Process according to Claim 1, wherein at least one other layer in the layer system is made of low refractive index material which is doped so that at a moment when the other layer is reached by the etching process, a change of emitted light radiation occurs which can be detected.
17. Process according to Claim 16, wherein the other layer is

doped with alkaline earth ions.

18. Process according to Claim 1, wherein the substrate comprises glass containing alkaline earth ions which changes in its emitted light radiation in a manner that can be detected, when a reactive glow discharge-enhanced etching process has reached the glass, the process including activating the gas using a reactive glow discharge.
19. Process according to Claim 1, including directing at least one light beam with a spectral range in which the structural element is light-transmitting, onto and through a side of the structural element which is not eroded to an opposite side of the structural element which is being eroded, some of the light being reflected, and drawing conclusions about a remaining coating thickness of material on the opposite side of the structural element from changes in the reflected light.
20. Process according to Claim 1, wherein

$$\text{Me} = \text{Y} \text{ and}$$

$$x = 1.5$$
 and consequently the layer is Y_2O_3 .
21. Process according Claim 1, including using for the etching of the MeO_x layer a fluorine-containing gas.
22. Optical element which is built up from a carrier substrate and at least one dielectric layer with at least two regions which are stepped with respect to their thickness, the optical element comprising:
the layer being a material of type MeO_x where

M is a metal of at least mass 44,
 x is selected so that the layer material for light of
 wavelength $\lambda = 308 \text{ nm}$ has a coefficient of absorption k

$$k_{308} \leq 0.01$$

and the thickness step has been created by a reactive ion
 etching process.

23. Optical element Claim 22, wherein $k_{308} \leq 0.003$.
24. Optical element according to Claim 22, made according to
 the process comprising:
 applying the dielectric layer of MeO_x onto a base of
 the substrate, Me being a metal whose atomic mass is
 at least 44, x being selected so that the
 coefficient of absorption k of the layer material at
 light of wavelength $\lambda = 308 \text{ nm}$ is
 $k_{308} \leq 0.01$; and
 building up the layer system using reactive etching
 by means of an activated gas to form the step in
 thickness in the dielectric layer.
25. Optical element according to Claim 22, wherein for at
 least one of the layers:
 $\text{Me} = \text{Ta}$ and $x = 2.5$.
26. Optical element according to Claim 22, wherein for at
 least one of the layers:
 $\text{Me} = \text{Hf}$ and $x = 2$.
27. Optical element according to Claim 22, including at least
 one region of reduced thickness which does not vanish in
 the layer thickness.

28. Optical element according to Claim 22, wherein the at least one layer is a part of a layer stack applied on the substrate, and including in addition to the at least one layer, at least one additional layer of low refractive index selected from the group comprising SiO_2 and Al_2O_3 .

29. Optical element according to Claims 22, for at least one layer applies:

$$\text{Me} = \text{Y}$$

$$x = 1.5.$$

30. An optical imaging system including a UV laser beam source and a mask through which UV light from the source passes for modulation of the laser beam, the mask being an optical element built up from a carrier substrate and at least one dielectric layer with at least two regions which are stepped with respect to their thickness, the layer being a material of type MeO_x where

Me is a metal of at least mass 44,

x is selected so that the layer material for light of wavelength $\lambda = 308 \text{ nm}$ has a coefficient of absorption k

$$k_{308} \leq 0.01$$

and the thickness step has been created by a reactive ion etching process.

31. An optical imaging system according to Claim 30, wherein the laser source outputs a beam energy density of more than 200 mJ/cm^2 .

32. A vacuum treatment installation for the fabrication of a structural element which is built up from a carrier substrate and at least one dielectric layer with at least

two regions which are stepped with respect to their thickness, the layer being a material of type MeO_x where Me is a metal of at least mass 44, x is selected so that the layer material for light of wavelength $\lambda = 308 \text{ nm}$ has a coefficient of absorption k where $k_{308} \leq 0.01$ and the thickness step has been created by a reactive ion etching process, the installation comprising:

means defining a vacuum chamber;
 a substrate carrier electrode;
 a counter-electrode for action with said carrier electrode;
 an ac voltage generator connected between said substrate carrier electrode and said counter-electrode; and

wherein said counter-electrode comprises an arrangement of distributed gas outlet openings for a reactive gas directed substantially toward said carrier electrode.

33. A vacuum treatment installation according to Claim 32, wherein the openings are regularly distributed on the counter-electrode.
34. A vacuum treatment installation according to Claim 32, including means for cooling the counter-electrode.
35. A vacuum treatment installation according to Claim 32, including a first arrangement for transmitting a light beam at an angle through the substrate carrier electrode to a substrate supporting surface of the carrier electrode and through the substrate, the light beam terminating at a surface of the substrate opposite from the carrier electrode, and a second arrangement for transmitting a light beam through the carrier electrode, the first

arrangement being connected to a light source, the second arrangement being connected to an evaluation unit for evaluating the light beam received through the second arrangement.

- 5 36. A vacuum treatment installation according to Claim 35, wherein at least one of the arrangements comprises a waveguide.
37. A vacuum treatment installation according to Claim 35, wherein both said arrangements are formed by one and the same light transmitter channel in the carrier electrode, which extends substantially perpendicularly to the substrate carrier surface of the carrier electrode.
38. A vacuum treatment installation according to Claim 32, including a throughflow setting element connected to the arrangement of distributed outlet openings, a tank containing CHClF_2 , connected to the throughflow setting element and at least one additional tank containing at least one of the gases selected from the group consisting of He, CHF_3 , and H_2 , connected to the throughflow setting element.
39. A vacuum treatment installation according to Claim 32, including a tank of gas comprising Cl_2 and a tank of another gas both connected to the arrangement of distributed outlet openings by a connection which is adjustable.
40. A vacuum treatment installation according to Claim 32, including a detector arrangement which outputs different signals for different surfaces exposed to the etching

process, and an evaluation unit for evaluating the different signals, and an adjustable connection between the arrangement of distributed outlet openings and at least one tank for supplying the gas, the connection being controlled by the evaluation unit according to the signals.

41. A vacuum treatment installation according to Claim 35, wherein an output of the evaluation unit controls the composition of the gas supplied to the gas outlet openings.
42. A vacuum treatment installation according to Claim 32, including an evaluation unit having an output for signals that are different for different surfaces exposed to the etching process, the evaluation unit being connected to at least one of the ac voltage generator and a setting element for a feeding of the gas the outlet openings.
43. A process for tracking an erosion or deposition of material from and to a treated side of at least one structural element transmitting in a given spectral range during the erosion or deposition, the structural element having an opposite untreated side and a thickness between the treated and untreated sides, the process comprising: guiding at least one light beam in said spectral range from the untreated side of the structural element onto and through the structural element to form a reflected light beam, and drawing conclusions about an instantaneous thickness of the structural element from changes of the reflected light beam.
44. A vacuum treatment installation for the deposition or

erosion of material from the surface of at least one work piece which is transmitting in a given spectral range, with a work piece carrier having a carrier surface upon which rests a work piece with a surface not to be treated, comprising: at least one first light transmitting arrangement extending through the carrier and terminating at the carrier surface, a light source communicating with the first arrangement, a second light transmitting arrangement extending through the carrier, and an evaluation unit for the evaluation of the light beam received through said second arrangement connected to the second arrangement, both the first and second arrangement being formed by one and the same transmission path which is substantially perpendicularly to the carrier surface.

45. Process for determining the point at which a given surface has been reached through a reactive etching of at least one superjacent layer in a process volume, comprising: doping the given surface with alkaline earth ions and detecting the point at which the surface is reached by the etching process by detecting the occurrence of a light of a given spectral range in the process volume.

46. Process according to Claim 45, wherein the given surface is formed by a substrate comprising glass with alkaline earth ions.

47. Process for controlling a reactive etching process of a layer stack with at least one first layer of high refractive index material and, above it, a second layer of low refractive index material, the first layer being MeO_x , Me being a metal whose atomic mass is at least 44, x being selected so that the coefficient of absorption k of the

- 37 -

layer material at light of wavelength $\lambda = 308 \text{ nm}$ is $K_{308} \leq 0.01$, the second layer being SiO_2 , the process comprising: etching the second layer using a gas without a Cl_2 fraction, the point at which the surface of the first layer is reached being detected and subsequently using another gas which has a Cl_2 fraction, for further etching.

5 48. An optical element comprising a layer system structured by reactive ion-etching and at least one layer being doped with alkaline earth ions.

10 49. An optical element according to Claim 48, wherein the layer is formed by a substrate comprising glass with alkaline earth ions.

50. In a reactive etching process using an Y_2O_3 layer as stop layer.

15 51. The process of Claim 50 including using as an etching gas in the process, CHClF_2 and He.

52. A process for the fabrication of a structural element substantially as hereinbefore described with reference to, and as illustrated by, the accompanying drawings.

20 53. An optical element substantially as hereinbefore described with reference to, and as illustrated by, Fig. 3 of the accompanying drawings.

25 54. An optical imaging system substantially as hereinbefore described with reference to, and as illustrated by, Fig. 4 of the accompanying drawings.

55. A vacuum treatment installation as claimed in Claim 32 or Claim 44 and substantially as hereinbefore described with reference to, and as illustrated by, the accompanying drawings.

30 56. A process for tracking erosion or deposition of material substantially as hereinbefore described with reference to, and as illustrated by, the accompanying drawings.

35

57. A process for determining the point at which a given surface has been reached during a reactive etching operation, the process being substantially as hereinbefore described with reference to, and as illustrated by, the accompanying drawings.

58. An etching process control method substantially as hereinbefore described with reference to, and as illustrated by, the accompanying drawings.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

- 39 -

Application number
 GB 9314993.8

Relevant Technical Fields

- (i) UK Cl (Ed.L) - B6J
 (ii) Int Cl (Ed.5) G03F

Search Examiner
 R J MIRAMS

Date of completion of Search
 18 October 1993

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
 1 to 3/

(ii) On-line databases: WPI Claims

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).